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Electrochemical Amination. Selective Introduction of Two Amino Groups into an Aromatic Ring

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Abstract—Indirect cathodic amination of anisole via a Ti(IV)–NH_2OH system in aqueous solutions of sulfuric acid is studied. The major products of the radical cation substitution in these media are *para*- and *ortho*-anisidines and 4-methoxy-1,3-phenylenediamine. The most efficient electrochemical process takes place in 10–12 M H_2SO_4. Under these conditions, complete conversion of the source of amino radicals is observed, and the total current yields, which correspond to the yields per hydroxylamine, reach 60%.

Keywords: cathode, Ti(IV)/Ti(III) mediator system, hydroxylamine, anisole, radical cation aromatic substitution, 4-methoxy-1,3-phenylenediamine

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The chemical amination of aromatic substrates with hydroxylamine and transition metal compounds in acidic aqueous and aqueous-organic media most commonly form isomeric monoamino derivatives as major products [1–9]. Electrochemical functionalization in dilute sulfuric acid solutions gives the same results [10–13]. However, in catholytes with H_2SO_4 concentrations higher than 7 M, a deeper substitution takes place, specifically, diamino derivatives are formed in significant amounts along with monosubstitution products [12, 13].

Until now consecutive introduction of two amino groups to the aromatic ring has been studied with only one substrate, namely benzene [12, 13]. The goal of the present work was to find out how the acidity of the sulfuric acid electrolyte affects the results of amination of anisole, a compound containing a substituent that makes the aromatic ring more reactive toward amino radical cations.

The electrolysis of the Ti(IV)–NH_2OH–C_6H_5OMe system was performed in 1.5–15 M aqueous H_2SO_4 under conditions favoring the synthesis of isomeric anisidines in aqueous-organic electrolytes containing sulfuric acid [14, 15]. Anisole was taken in a large excess with respect to hydroxylamine (0.046 and 0.005 mol, respectively), and, therefore, as the main substitution efficiency criterion we used the total current yield of amino compounds. Unlike the conditions used in [12, 13] for benzene amination, the quantity of electricity passed through the catholyte (482.4 C) was enough for not only partial, but also for complete theoretical conversion of hydroxylamine, based on the consumption of one electron per hydroxylamine molecule. To prevent electrochemical release of hydrogen in 1.5–10 M H_2SO_4 solutions we used a mercury cathode, and, in more acidic media, when mercury can be oxidized by Ti(IV), a platinum electron was used.

The amination of anisole in 1.5 M H_2SO_4 gives not only isomeric anisidines, but also 4-methoxy-1,3-phenylenediamine **1**. The current yields of anisidines and diamine **1** at 20°C are 5.9 and 1.6%, respectively (Fig. 1a). As the H_2SO_4 concentration is increased up to 4.5 M, the total substitution efficiency decreases (Fig. 1b). The decrease of the amination yield is associated with fact that reaction (1) involves exclusively the unprotonated form of hydroxylamine [12, 13], and the concentration of this form decreases upon the increase of the acidity of the electrolyte. Increasing concentration of Ti(III) generated both on the cathode and by methoxyaminocyclohexadienyl radical cations with Ti(IV) increases the fraction of